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Risø-M-2786

Annual Report 1988

Chemistry Department

**Edited by Jytte Funck, Aase Neve Larsen, Elfinn Larsen
and Ole J. Nielsen**

**Risø National Laboratory, DK-4000 Roskilde, Denmark
April 1989**

RISØ-M-2786

**ANNUAL REPORT 1988
CHEMISTRY DEPARTMENT**

Edited by Jytte Funck, Aase Neve Larsen, Elfinn Larsen and Ole J. Nielsen

Abstract. This report contains a brief survey of the main activities in the Chemistry Department. The names and abstracts of all articles and reports published and lectures given in 1988 are presented. The facilities and equipment are mentioned briefly. The activities are divided into the following groups: radioisotope chemistry, analytical- and organic chemistry, environmental chemistry, polymer chemistry, chemical reactivity, mineral processing, and general.

**April 1989
Risø National Laboratory, DK-4000 Roskilde, Denmark.**

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Grafisk Service Risø 1989

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This report contains a brief survey of the main activities in 1988 in the Chemistry Department including a listing of all articles and reports published and lectures given. The facilities and equipment are mentioned briefly.

The activities are divided into seven groups:

- 1. Radioisotope Chemistry**
- 2. Analytical- and Organic Chemistry**
- 3. Environmental Chemistry**
- 4. Polymer Chemistry**
- 5. Chemical Reactivity**
- 6. Mineral Processing**
- 7. General**

MAIN ACTIVITIES

1. RADIOISOTOPE CHEMISTRY

Part of the work in radioisotope chemistry continues to be performed in collaboration with researchers in the medical, geological, and archaeological fields from universities and hospitals. Certification work for the EEC Community Bureau of Reference continues to be a major effort. Papers on activation analysis and other methods of trace analysis were presented at several international conferences.

A patent is still pending, based on a post-graduate study, made in co-operation with the Technical University of Denmark (DTH) of the counting of rapidly decaying radioactive indicators.

In collaboration with the Agricultural University and Odense University Hospital, activation analyses have been used to determine Na, K, Mn, Zn, Cr, Fe, Zn in lyophilized food as a quality control procedure for a more complete analysis by ICP/MS.

In collaboration with the Niels Bohr Institute, the production of ^{153}Gd has continued on a smaller scale as the demand for sources has been lower than predicted.

Industrial irradiation of silicon has remained constant with practically full utilisation of all irradiation facilities. Construction of a new, horizontal facility for silicon ingots up to 5" diameter is under way. This facility will improve the quality of the irradiation. A full-scale model has been built to test various ways to control the exact neutron fluence.

At the First Scandinavian Conference on Chemometry in Finland, multivariate data analysis of results obtained by instrumental neutron activation analysis of Mesopotamian ceramics and clay was presented. This work was carried out in co-operation with the Carsten Niebuhr Institute and was supported by the Research Council for the Humanities; the results did not support existing hypotheses for the development of trade in the Middle East from about 5000 years ago, but have generated several new ideas of archaeological interest.



Fig. 1.1. 5" silicon ingots are loaded into a can of aluminium before irradiation.

Scientific Staff: Kaj Heydorn, Kirsten Andresen, Else Damsgaard, Ulf Jacobsen, Inge Overby Jensen, Jesper Jørgensen.

Technical Staff: Steen Bidstrup, Lene Birch, Jørgen Hanefeld-Møller, Jørgen Erik Hansen, Jette Iversen, Bente Jacobsen, Jytte Jakobsen, Bo Lars Jensen, Margit Elbek Jensen, Marianne Elsborg Jensen, Ole Bauer Johansen, Svend-Erik Kerchhoff, Maibritt Kringel Kristiansen, Merete Larsen, Leif Lauersen, Kirsten Madsen, Gitte Rasmussen, Søren Walbom Sørensen, Mette Thomsen, Børge Valentiner.

Consultant: Leif Højslet Christensen.

Guest Students: Henrik Bendiksen, The Technical University of Denmark
Soo-Kyung Rhee, Ehwa University, Seoul.

Guest Scientist: Natan Lavi, Soreq Nuclear Research Centre, Israel.

2. ANALYTICAL- AND ORGANIC CHEMISTRY

On December 2nd, the group celebrated the tenth anniversary of the recording of the first collision-induced decomposition mass spectrum. The experiment was the first of its kind in Scandinavia. During the past decade the application of the technique has grown rapidly and is now an important tool in solving analytical problems.

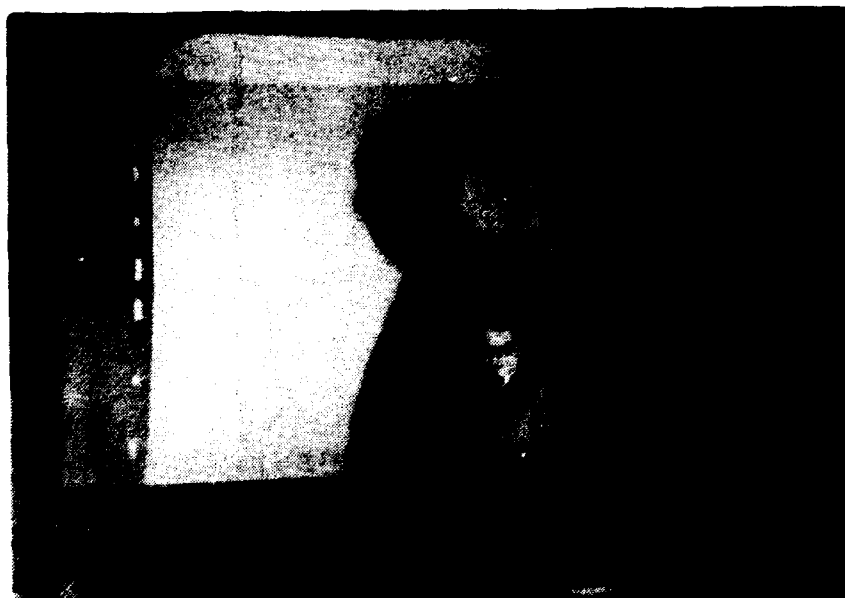


Fig. 2.1. Jørgen Møller, Odense University, gave the gala-lecture.

The group participated in the GENIUS (Geochemical Exploration by analysis of Nitrogen Isotopes in Undisturbed Sea bed samples) project with gas extraction, gas analyses and nitrogen isotope analyses. The project is completed and a final report will be prepared by Danpec Aps and Cowiconsult.

The **Laboratory for Hydrocarbon Characterization** has continued to develop the experimental characterization of petroleum fractions. Co-operation has been initiated with the PVT-laboratory and the Laboratory for Energy, both in DTH, in order to establish a Danish PVT-group and a petroleum laboratory. The group has applied to EFP-89 for a project on "Measurement and Correlation of the PVT-properties of Oil and Gas From Danish Reservoirs". Furthermore, the group has been in contact with AGIP and is now analyzing several Italian crudes.

In 1988 the laboratory continued its participation in the basin modelling project BASMOD (DGU, DOPAS, and RISØ) and has contributed to the source rock evaluation in the Central Trough. Biomarker depth-profiles have been analyzed for several wells, and this work will be continued to complete the regional study of the Central Trough. A similar study has been initiated for North Jutland.

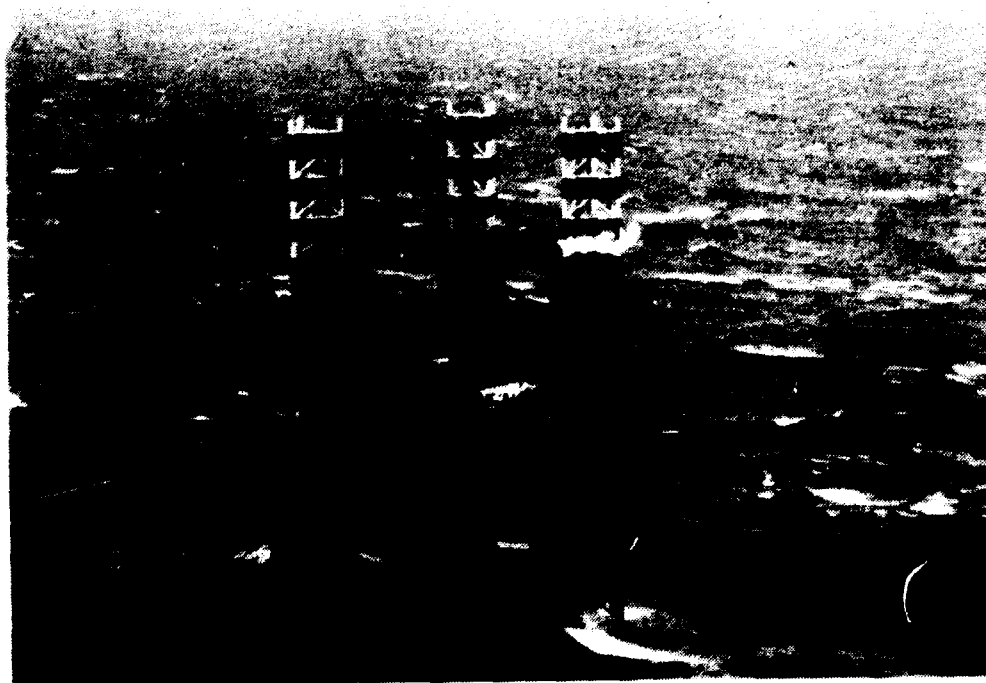


Fig. 2.2. The Mærsk Guardian Drilling Rig in the North Sea.

In 1988 a three-day analysis program was performed at the Mærsk Guardian Drilling Rig in the North Sea (Fig.2.2) to monitor air-borne particles and aerosols in the Shale Shaker House. Data are being analysed for, among other reasons, to clarify if any health hazards were present during drilling operations.

Studies of ionic species isolated in the gas phase and organic high-temperature chemistry are the two main research areas in the field of physical-organic chemistry.



Fig. 2.3. The Orion Nebula. Reaction between imidcgen and carbon.

The activities within ion chemistry have been concentrated on studies of closed-shell cations. As a result of these studies novel species such as H_3CO_3^+ and H_3SO_3^+ may now be recognized as well as characterized. In addition, the possible quantum-mechanical tunnelling of the methylnitrite radical cation was elucidated by combined ^2H - and ^{18}O -labelling experiments.

Detailed studies of isolated ions relies heavily on the application of stable isotopes including those of heavier elements as ^{18}O and ^{34}S . It appears that the group now benefits by the acquired expertise in the preparation and purification of labelled compounds.

The unique reactor-design applied for high-temperature studies has been further developed to include time-resolved experiments on intermediate species as e.g. "hot" acetaldehyde CH_3CHO^* .

The pyrolysis technique has been used to elucidate the reaction between the parent nitrene, imidogen, and elemental carbon. It is a reaction apparently highly relevant to combustion chemistry and astrochemistry (Fig. 2.3).

A study on particulate matter pyrolysis with the participation of University of Salt Lake City (funded by NATO) has been concluded. The result demonstrated that pyrolysis is a potentially powerful technique for particulate matter characterization.

The Mineral Analysis Group has continued work with an EFP-86 project determining geochemical criteria for reservoir quality parameters by analysing drill core samples from the well E-1x. Interpretational work has been initiated and the project will terminate in 1989 with a final report.

A new energy-research project within the framework of EFP-88 has been started in 1988. By using fission-track analysis of apatite in samples from Danish sedimentary basins (Central Graben area and Danish Subbasin), paleo-heat flux estimates are envisaged. Such basin temperature-time estimates are important in basin modelling and source rock alteration studies (kerogen production). The project is a co-operative effort with the Risø Energy Technology Department, University of Copenhagen (Institute of Petrology) and Geological Survey of Denmark. Work will continue until 1990.

The research group continued co-operation on marine environmental work with the Hamburg and Kiel universities, which also included geochemical studies on marine minerals. Contact has been established

with Woods Hole Oceanographic Institution in Massachusetts, USA, and co-operation exists with the New Zealand Oceanographic Institute.

A joint evaluation of possible offshore marine minerals in Greenland waters has been carried with the Geological Survey of Greenland and these results were presented at the 19th Underwater Mining Institute (USA).

Applied geochemical projects involving analytical and evaluation input were continued with Galway University College (Ireland) and the Geological Survey of Greenland.

Scientific Staff: Lars Carlsen, Asger Baltzer Hansen, Helmar Kunzendorf, Elfinn Larsen, Per Solgaard.

Technical Staff: Helge Egsgaard, Jytte Funck, Per Ingemann Jensen, Ole Jørgensen, Lis Vinther Kristensen, Birgit Petersen, Susanne Petersen, Poul Sørensen, Niels Vinther, Hanne Voss, Jonna I. Carstensen, Hanne Staugaard Nielsen, Jens Schoustrup-Thomsen, Ursula Marie Jacobsen.

Guest Student: Haruna Yoshimura, Waseda University, Tokyo.

Guest Scientists: W.H. McClennen, University of Utah, USA
M. Feely, K. Barton and Audy Sides, University College
Galway, Ireland
Susanne Elbel, University of Hamburg.

3. ENVIRONMENTAL CHEMISTRY

The main aim of the Environmental Chemistry group is to study fundamental chemical and physico-chemical processes in the terrestrial and atmospheric environment. Both experimental and theoretical activities take place.

The activities within the frame of the EC nuclear research programme have been continued during 1988. The studies comprised "The role of organics in the migration of radionuclides in the geosphere", "Geochemical modelling", "Geochemical databases", and "Artificial materials".

A study on enzymatically controlled iodination of natural occurring organics as humic acids has been initiated in the frame of a Ph.D. study.

In 1988 the Environmental Chemistry group has been involved in studies of polycyclic aromatic hydrocarbons (PAH) as a part of an air pollution study at Copenhagen airport.

Knowledge in the area of ecotoxicology was founded during the work with the former uranium project in Greenland. This knowledge is now used in connection with other mining projects in Greenland. In addition, ecological investigations are carried out in order to assess the general effects in the environment and establish emission criteria. The work is funded both by public and private sources.

Within the frame of the Environmental Chemistry Group, a facility has been built to study hydrocarbon formation from coals and kerogens, based on pyrolysis gas chromatography. The studies on solid state kinetics have been financed by the Danish Department of Energy through the EFP-project.

September 6.-8. the Chemistry Department hosted the 4th plenary meeting of the EC project group CHEMVAL with 25 participants from 8 countries.

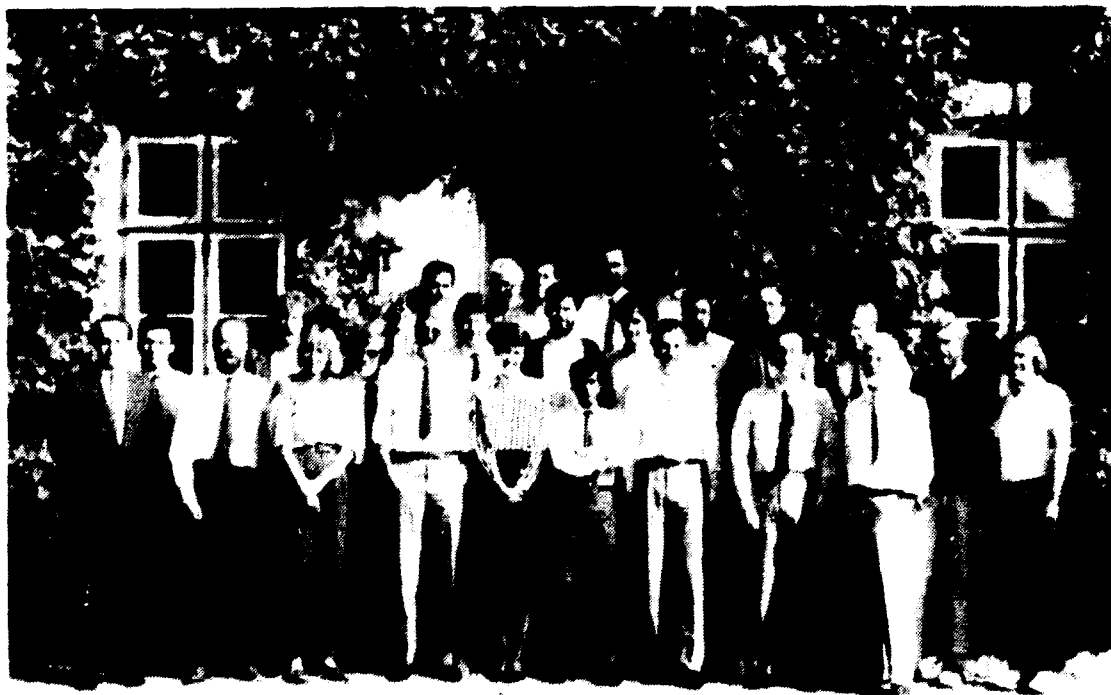


Fig. 3.1. The participants of 4th plenary CHEMVAL meeting at Svaleholm, Risø, Sept. 1988.

Scientific Staff: Peter Bo, Knud Brodersen, Lars Carlsen, Bror Skytte Jensen, Ole John Nielsen, Torben Nielsen, Karen Nilsson, Kim Pilegaard

and Jesper Valentin Christiansen.

Technical Staff: Anders Feldthus, Hanne Jensen, Gitte Larsen, Anne B. Nielsen, Jesper B. Rasmussen and Arne Vinther, Ingrid Pedersen.

4. POLYMER CHEMISTRY

Different chromatographic techniques have been used for characterizing low as well as high molecular mass materials. The determination of molecular masses of water-soluble polymers using the low-angle laser light scattering (LALLS) detector is still an important activity. The limitations in the use of LALLS for absolute molecular mass determinations have been investigated both from a theoretical and an experimental point of view.

High-vacuum techniques for synthesis of extremely high molecular mass polymers with narrow molecular mass distribution have been developed.

Models of rubber elasticity and polymer chain dynamics have been compared with stress-strain and rheological data.

Work on comb-shaped polyesters has progressed with the preparation and characterization (DSC, ^{13}C NMR, and SEC) of an extended range of diphenyl esters of aliphatic carboxylic acids. Optimal polycondensation techniques have resulted in polyesters with molecular masses three times greater than hitherto reported in literature, allowing oriented films and fibers to be produced.

Actin and fibrinogen polymerization and gel formation have been studied by use of our rheometers. A new model for actin elasticity has resulted from the rheological studies of actin and actin-binding proteins. The properties of fibrin clots are sensitive to the presence of dextrans and platelets. The gel formation of well-characterized pectins are also studied. Insulin association and tropomyosin thermal stability are investigated by use of LALLS and circular dichroism.

The mechanical spectrometers RMS 800 and RFS 8500 have been used in studies of polymer blends, composite materials, thermoplastic polymers, drilling mud, and solutions.

Scientific Staff: Kristoffer Almdal, Kurt Heller, Søren Hvidt, Søren Hvilsted, Ole Kramer, and Walther Batsberg Pedersen.

Technical Staff: Lotte Hansen and Lene Hubert.

Guest Scientists: Prof. Paul A. Janmey, Harvard Medical School.
 Prof. R.F.T. Stepto, UMIST, Manchester.
 Dr. Thomas Twardowski, University of Illinois.

5. CHEMICAL REACTIVITY

The main research activities in the section are chemical kinetics and spectroscopy. UV, IR and resonance Raman spectra of free radicals and molecules in excited states provide structural information on the short-lived reactive species, and they can be utilized in studies of chemical kinetics of elementary reactions. The section has two other research activities: Physical Dosimetry and Radiation Processing and Dosimetry. Physical Dosimetry was terminated as a research topic within the section by the end of 1988.

Gas phase group

Oxygenated hydrocarbon radicals are of great importance in combustion and atmospheric oxidation of hydrocarbons, and we have employed pulse radiolysis combined with time-resolved UV-spectroscopy in studies of the spectral and kinetic features of this radical. The ultraviolet spectrum is composed of several vibronic progressions extending over a range of 200-285 nm. Various Rydberg transitions have been identified on the basis of very detailed ab initio configuration studies of CH_2OH . Rates and mechanisms of several elementary reactions of CH_2OH have been studied, in particular the reaction with oxygen where we have identified two different product channels. The reaction of hydroxyl radicals with carbon monoxide is the most important source of carbon dioxide in combustion processes and the atmosphere. The reaction rate is pressure dependent, and we have studied the reaction at 140 atm where the adduct COOH is observed, while experiments at 1 atm show that the "hot adduct" splits up into $\text{H} + \text{CO}_2$. A new experimental technique based on pulse radiolysis combined with infrared diode laser spectroscopy has been employed in studies of a series of elementary reactions of methyl radicals. Work is in progress to determine the temperature dependence of the equilibrium constant for the metathetical reaction $\text{CH}_4 + \text{Cl} = \text{CH}_3 + \text{HCl}$. The aim of this study is to derive the reaction enthalpy and heat of formation of CH_3 .

The work on CH_2OH is done in collaboration with Christopher Anastasi, University of York and Sten Rettrup, Department of Physical Chemistry,

H.C. Ørsted Institute, University of Copenhagen.

In the first year of a four-year EC-funded (COST 611) collaboration with University College Dublin, investigations of the reactions of Cl and OH with nitroalkanes and organic sulphur compounds, RSR, (R = methyl-, ethyl-, n-propyl- and n-butyl-radicals) have been finished. Details of the results can be found in the first annual report (Risø-M2755). The international collaborations with Dr. Tim Wallington (Ford Motor Co, USA), Dr. Michael Kurylo (NBS, USA) and Dr. Roger Atkinson (SAPRC, USA) were continued.

The infrared-lineshape studies in collaboration with Flemming Nicolaisen at the University of Copenhagen were expanded.

Water phase group

The mechanism for the natural decay of ozone in aqueous solution is of great importance in raindrop chemistry. In the past year we have studied the reactions of hydrogen peroxide with ozone. We have shown that hydrogen peroxide is formed during ozone decay, and we also know that it enhances the ozone decay. The mechanism for the formation of hydrogen peroxide is not known, and the reactions with ozone are not completely understood. We have established that the formation of hydrogen peroxide is initiated either by the oxygen atom released from the dissociating ozone molecule or from an excited ozone molecule. Furthermore, we have established that not only HO_2^- but also H_2O_2 reacts with ozone.

The role of the ozone stabilizer, acetate, was also studied with reference to hydrogen peroxide reactions.

The work on reactions at high temperature and pressure has the purpose of obtaining thermodynamic data for elementary reactions in radical chemistry. The work was concentrated on determining the activation energies of the reactions $\text{OH} + \text{O}_2^-$ and $\text{H} + \text{H}$. Some work was also done on determining the radical scavenger effects at high temperatures.

Raman group

The main project was characterization of isomerization processes and excited electronic states in linear trienes. Our international collaboration with Prof. G. Orlandi (Bologna, Italy), Dr. A.M. Brouwer (Amsterdam, The Netherlands), and Dr. A.A. Gorman (Manchester, England) was continued. Theoretical calculations were performed on the potential energy surfaces of trienes in their ground state and first excited triplet state. Time-resolved resonance Raman spectra were recorded of deuterated and methylated hexatrienes. Two Ph.D. studies (B. Amstrup in

collaboration with Prof. J.P. Dahl, the Technical University of Denmark, and S. Møller in collaboration with Dr. F. Duus, Roskilde University) are in progress; the first deals with resonance Raman spectroscopy of hexatriene vapor and the second with triplet-state photochemistry of hexatriene.

Physical dosimetry

In collaborative work with Kjeld J. Olsen, University Hospital of Copenhagen, Herlev, efforts have been made for the purpose of developing a model that will predict recombination kinetics of radiation-induced free radicals in L-alpha-alanine following heavy charged-particle exposures. We have compared measured with predicted recombinations calculated as a function of particle and detector parameters, and agreement within the experimental uncertainty is achieved between experimental and calculated data. The work was supported by the Commission of the European Communities under Contract No. B1-6-0028-DK(B).

Radiation processing and dosimetry

Consulting, dose measurements, calibrations and measurements in connection with validation of radiation sterilization for customers in Denmark and abroad are becoming the major work areas. We are well suited for these tasks, particularly with regard to electron beam facilities. Many years experience in dosimetry combined with the radiation processing capacity have given us a position, which is utilized also in connection with national and international organizations (Danish Food Research Institute, CERN, IAEA).

A co-operation with National Physical Laboratory, UK, under the Euromet programme has led to the establishment of the water calorimeter as the reference for 10-MeV accelerators, traceable to the NPL. The water calorimeters that we use at Risø have been sold to other Danish facilities, as well as to Sweden, UK, and Hungary. The dichromate dosimeter, which is also established in Euromet collaboration with NPL, is now used as transfer dosimeter between Risø and NPL, and between Risø and commercial gamma facilities, thereby providing traceability.

The development of film dosimeters has not continued as quickly as had been hoped due to the increased commercial work, but the development is continuing of film dosimeters useful in validation and making routine measurements at the electron accelerator from 200 keV to 10 MeV.

Radiation processing is progressing, mainly at the 10-MeV linac, for sterilization and plastic modification. Small amounts of foods (spices) were also treated for decontamination. The collaboration with the

Polymer Group on development and implementation of new processes has continued in collaboration with Danish and foreign firms.

Scientific Staff: B. Amstrup, E. Bjergbakke, T. Ellerman, J. Fenger, J.W. Hansen, K.B. Hansen, J. Holcman, F.W. Langkilde, B. Lynggaard, A. Miller, S. Møller, O.J. Nielsen, P. Pagsberg, K. Sehested, A. Sillesen, R. Wilbrandt.

Technical Staff: H. Corfitzen, P. Genske, C. Hansen, E. Haugaard, T. Johansen, B. Kristiansen, E.E. Larsen, F. Larsen, M.B. Madsen, R. Madsen, J. Munk, K. Pejtersen, M. Wille, Annie S. Andersen.

Guest Scientists:

M.Sc. Denis O'Farrell, Dublin Institute of Technology, Ireland.
 M.Mc. Michael Donlon, Dublin Institute of Technology, Ireland.
 Dr. Howard Sidebottom, University College Dublin, Ireland.
 Dr. Donald Fitzmaurice, University College Dublin, Ireland.
 Prof. Emil Ratajczak, University of Wroclaw, Poland.
 Dr. Christopher Anastasi, University of York, England.
 Dr. Fabrizia Negri, Dipartimento di Chimica, Bologna, Italy.
 Dr. Krzysztof Bajdor, Polish Academy of Sciences, Warsaw, Poland.
 Dr. E.J. Hart, Port Angeles, USA.
 Dr. Krzysztof Brobowski, Polish Academy of Sciences, Warsaw, Poland.
 Prof. Nikola Getoff, University of Vienna, Austria.
 Dr. Sonja Solar, University of Vienna, Austria.
 Prof. Joseph Rabani, Hebrew University, Jerusalem, Israel.
 Dr. Andras Kovacs, Institute of Radioisotopes, Budapest, Hungary.
 Dr. Hilbert Christensen, Studsvik Energiteknik AB, Nyköping, Sweden.
 M.Sc. Ulrik Kläning, University of Århus, Denmark.
 Ms. Siriratana Biramontri, Office of Atomic Energy for Peace, Bangkok, Thailand.
 Dr. William L. McLaughlin, National Institute of Standards and Technology, Gaithersburg, USA.

6. MINERAL PROCESSING

The group has been working mainly with the implementation of the wet oxidation process on a semi-industrial scale. After studying the reactions in a bench autoclave, we have adapted the pilot plant pipe reactor to accept a suspension of clayey soil. The sample, which was provided by Nordic Cable and Wire A/S (NKT), came from a former tar distillation site and was heavily contaminated by naphthalene, phenantrene, and other polycyclic compounds. The chemical purification was very promising.

Problems with material handling and filtration turned up, but were satisfactorily solved.

A study on the stability of asbestos has been carried out in collaboration with B. Skytte Jensen for the Danish Environmental Protection Agency. The routes of conversion have been calculated on the basis of thermodynamic data, and in the laboratory the decomposition has been studied under both mild and forced conditions.

A review of the zirconia recovery from eudialyte has been made in anticipation of the coming Center for Advanced Ceramics.

Finally, the work on soil recovery has prompted an investigation of intermediates and pretended end product from the wet oxidation of toxic compounds.

Scientific Staff: Jørgen Jensen, Emil Sørensen, Torkild Lundgaard, and Belinda Bjerre.

Technical Staff: Helle Krogh, Jette Fosskov, Sv.Kr. Olsen, and Thomas Fernquist.

7. GENERAL

The Department accomplishes chemical analyses and services for other departments at Risø, and on a commercial basis for external customers.

The Isotope Laboratory has continued to fulfil its commitment as the sole producer of neutron-irradiated materials for technical and scientific purposes in Denmark. The collaboration with the Isotope Pharmacy has proceeded in the production of radiopharmaceuticals for medical diagnostics, and in November the license required for producers of radiopharmaceuticals was renewed for another five-year period by the National Board of Health. Radioisotope production mainly for scientific research has continued, and ^{60}Co sources for liquid-level measurements in cylinders containing liquified gas are produced.

As a supplement to the α , β and γ demonstration sources for educational purposes, supplied to the Nordic countries, a ^{226}Ra sources for continuous cloud chambers is available and these four sources have also been approved by the authorities in Austria for educational purposes.

The handling and disposal of radioactive wastes from Risø and other

users of radioactive isotopes are taken care of at The Waste Treatment Plant.

In March The Accelerator Department and Chemistry Department were fused.

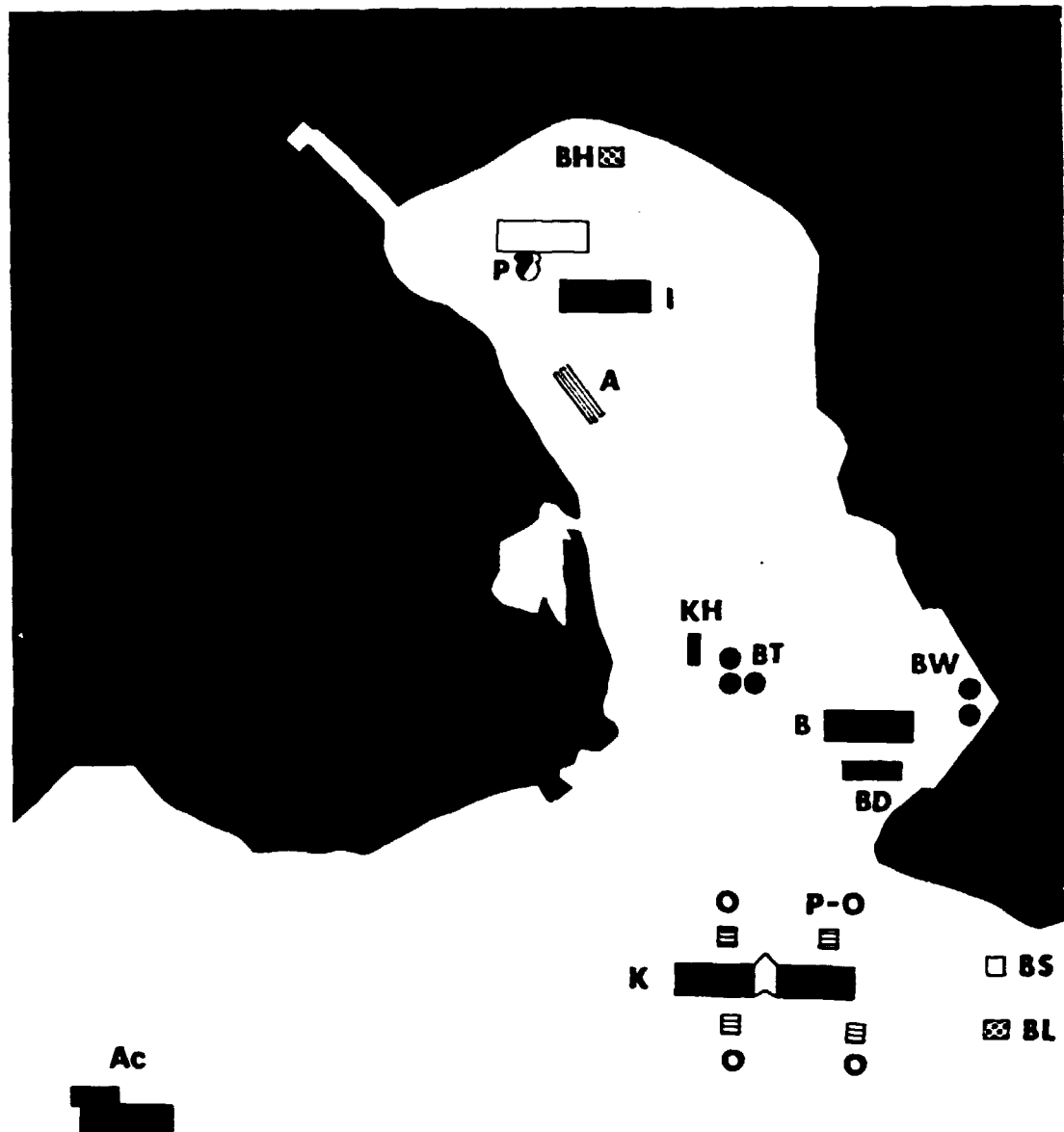
A technical staff takes care of purchase, stocks, administration, typing, workshop, laundry, radioactive cleaning, etc.: Aase Neve Larsen, Kirsten Bay, Jytte Green, Ellen M. Jensen, Ester Andersen, Inger Jakobsen, Fini Lindskou, Svend Nielsen, Knud Larsen, Erling Christensen, Bent Villumsen, O. Sølling Hansen, Bent Nielsen, Jørgen Larsen, Svend Jensen, Signe Hansen, Birthe I. Hansen, Birthe N. Andersen, Pedro Breschiani, Ruth Ågensen, Palle Olsson, Winnie Andersen, Nina Thomsen.

Risø's Chemistry Department includes five geographically separated sections: The Chemical Laboratory, The Accelerator Department, The Radioisotope Laboratory, The Waste Treatment Plant, and The Mineral Processing Plant.

The staff of the department consists of 35 members with academic degrees, 3 Ph.D. students, and 70 technicians, including office personnel.



Fig. 7.1 Celebration of the fusion with The Accelerator Department.



- | | |
|--|--|
| K Kemi Huse. The Chemical Laboratory | BS Shredder and Controlled Dump Site for Inactive Waste |
| O Office Annex | BL Storage for Waste with Low Radiation |
| I Isotoplaboratorium. The Radioisotope Laboratory | BH Storage for Waste with High Radiation |
| B Behandlingsstationen. The Waste Treatment Plant | P Procesterkem. The Mineral Processing Plant |
| BD Drum Storage | KH Grinding Equipment |
| BW Waste Water Treatment | A Pipe Autoclave |
| BT Storage Ponds for Uranium Mine Tailings | Ac Accelerator. Chemical Reactivity |

NEUTRON ACTIVATION ANALYSIS

K.Heydorn

in: ENCYCLOPEDIA OF MEDICAL DEVICES AND INSTRUMENTATION

Vol. 3 Ed. by John G.Webster

John Wiley and Sons, New York 1988, 2041 - 2046

Applications of neutron activation analysis in fundamental, biological investigations, as well as in clinical research and development, continue to appear in the literature. Elements not studied previously, such as the noble metals and the rare earth elements, are now attracting attention.

Neutron activation analysis may never be established as a practical routine method for biological application, not only because of the need for a nuclear reactor, but also because of the comparatively long time needed to carry out NAA. Its leading role, however, as a scientific tool for the highest analytical requirements, including the exploration of normal values for new elements, is likely to remain unchallenged in the future. Neutron activation analysis will continue to be used when other methods fail.

RADIOCHEMICAL METHODS FOR SELENIUM IN BIOLOGICAL MATERIALS

Kaj Heydorn

Trans. Am. Nucl. Soc. (1988) 56, 152

RESENT DEVELOPMENTS IN NUCLEAR ACTIVATION ANALYSIS

K.Heydorn

Isotopenpraxis 24 (1988) 2, 45 - 48

On the basis of papers presented at the 7th International Conference on Modern Trends in Activation Analysis held in Copenhagen, Denmark, 23—27 June 1986 an attempt is made to evaluate future trends in the field of nuclear activation analysis. The diversity of applications and the significant improvements in methodology are highlighted in this review.

CLASSICAL PITFALLS IN CONTEMPORARY NUCLEAR DATA ANALYSIS

K.Heydorn

Journal of Research of the National Bureau of Standards
Accuracy in Trace Analysis

Vol. 93, No. 3 May - June (1988) 479 - 480

NEUTRON TRANSMUTATION DOPING OF SILICON AT RISØ NATIONAL LABORATORY

K.Heydorn and K.Andresen

In: Silicon Transmutation Doping Techniques and Practices.

Proceedings. Otwo'k - Swierk, 20 - 22 Nov. 1985

IAEA - TECDOC - 456 (1988), 17 - 27

Irradiation of silicon single crystals with both thermal and fast neutrons began at the Risø National Laboratory in 1960. The first industrial irradiations were performed in the thermal column at the DR-2. The present facility is installed in the heavy water research reactor DR-3 and is capable of irradiating 4 inch diameter crystals. The paper describes three generations of neutron transmutation doping facilities at the laboratory.

MULTI - ELEMENT ANALYSIS

R.Cornelis, K.Heydorn, G.F.Nordberg

In: Trace Elements in Human Health and Disease.

The 2nd Nordic Symposium. Odense 17 - 21 Aug. 1987

Ed. by. P.Grandjean

Environmental Health Series 26, 28 - 30

Multi-element analysis is the simultaneous determination of several elements in the same sample.

CLINICAL USE OF TRACE ELEMENT ANALYSIS

R.A.Braithwaite, K.Heydorn and M.Hørder

In: Trace Elements in Human Health and Disease.

The 2nd Nordic Symposium. Odense 17 - 21 Aug. 1987

Ed. by. P.Grandjean

Environmental Health Series 26, 106 - 110

Trace elements are present in the human body in amounts below 100 mg/kg. Some trace elements are known to be essential for the maintenance of human growth and homeostasis, and for some no role for human health has yet been established. With regard to clinical application of trace element analyses, six problem areas may be defined.

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS TECHNIQUE USING SUBSECOND RADIONUCLIDES

H.K.Nielsen and J.O.Schmidt

Journal of Radioanalytical and Nuclear Chemistry, Articles,

Vol. 114, No 2 (1987) 237 - 241

The fast irradiation facility Mach-1 installed at the Danish DR 3 reactor has been used in boron determinations by means of Instrumental Neutron Activation Analysis using ^{12}B with 20-ms half-life. The performance characteristics of the system are presented and boron determinations of NBS standard reference materials as well as fertilizer materials are compared by literature value and spectrophotometric measurements, respectively. In both cases good agreement is obtained.

VERIFICATION TESTING OF COMMERCIALY AVAILABLE COMPUTER PROGRAMS FOR PHOTOPEAK AREA EVALUATION

THE INFLUENCE OF PEAK WIDTH

K.Heydorn and L.H.Christensen

Journal of Radioanalytical and Nuclear Chemistry, Articles, 124 No.2
(1988) 467 - 480

Computer programs available from three major manufacturers of systems for γ -ray spectrometry were tested by measuring the same ^{152}Eu source under nearly identical conditions. Results for the evaluation of peaks with full widths at half maximum ranging from less than 3 and up to 15 channels were compared with those obtained by a reference program based on peak integration using optimum peak boundary selection. Two out of three commercial programs produced results without significant influence of peak width, but none of them could maintain the same level of statistical control throughout the range of interest that the reference program does.

DISTRIBUTION OF URANIUM IN TWO SULPHIDE ORE ENVIRONMENTS FROM THE REVERSED METAMORPHIC SEQUENCE OF THE DALING ROCKS IN THE DARJEELING-SIKKIM HIMALAYA, INDIA

A.K.Ghosh and H.Kunzendorf

Uranium, 4 (1988) 341 - 349

In the low-grade Daling metasediments of Gorubathan, the average U content of 3-4 ppm reflects the original U content of the unmetamorphosed sediments. The high-grade metasediments of Dikchu average 6 ppm, and the sulphide ores of this area also have more U compared to Gorubathan ores. This higher U content in the high-grade rocks and in the associated ores is believed to be the result of enrichment during metasomatic activity in the area.

Nevertheless, the fact that the Daling metasediments have higher U contents than that of the sulphide ores appears to be independent of the grade of metamorphism in the progressive sequence.

PROPOSED MARINE MINERAL EXPLORATION STRATEGIES FOR THE NINETIES

Helmar Kunzendorf

Marine Mining, 7 (1988) 233 - 247

Marine mineral exploration is a relatively new research area combining a wide variety of geosciences disciplines to discover and describe marine mineral occurrences. Adopting terrestrial mineral exploration strategies, this paper describes the marine mineral exploration techniques developed over the past decades. Marine mineral commodities are mentioned briefly; marine exploration geophysics and exploration geochemistry are discussed, as are the techniques of data interpretation. Finally, the most important new techniques in the years to come are outlined.

IRIDIUM-BEARING CARBON BLACK AT THE CRETACEOUS-TERTIARY BOUNDARY

H.J.Hansen, K.L.Rasmussen, R.Gwozdz and H.Kunzendorf

Bulletin of the Geological Society of Denmark, 36 (1987) 305 - 314

Carbon black has been observed to be the staining agent of the 3.5 m grey chalk underlying the Fish Clay in the Stevns Klint section. We show that carbon black extracted from the grey chalk and Fish Clay has a carbon isotope value significantly different both from the underlying Upper Cretaceous carbon black and from that of Upper Cretaceous charcoal. Carbon black stained bryozoan skeletons in the grey chalk are often seen to encrust on non-stained bryozoan skeletons and *vice versa* in the same stratigraphic level. This indicates that carbon black deposition took place in pulses during the ca. 50,000 year long grey chalk time interval. The carbon black-stained bryozoan skeletons are found to be rich in Ir as well as in other elements, and we demonstrate that the Ir-carrying phase is not a silicate, but rather the carbon black itself. A volcanic origin is suggested for the Ir-bearing carbon black.

CHEMICAL COMPOSITION OF MANGANESE NODULES

Günther Friedrich, Walter L.Plüger and Helmar Kunzendorf

In: The Manganese Nodule Belt of the Pacific Ocean

Geological Environment, Nodule Formation and Mining Aspects

Ed. by Peter Halbach, Günther Friedrich and Ulrich von Stackelberg

Ferdinand Enke Verlag, Stuttgart (1988) p. 37

EXPERIMENTAL SAMPLE CLASSIFICATION AND OPTIMAL MEASUREMENT CONDITIONS IN SHORT-TIME INAA

R.Gwozdz, J.O.Schmidt and H.Kunzendorf

J.Trace and Microprobe Techniques, 6 (3), (1988), 401-416

A simple prediction program for determination of the detection limit based on the single comparator method was prepared for use with a personal computer. The program was tested and used together with a set of about 200 measurements of different standard samples irradiated 10 to 60 seconds, and measured after 5 to 1000 minutes decay time. In order to compare the experimental results to those calculated, three new expressions were introduced; a figure of merit, an adjustment factor and a deterioration factor.

PURPURIC CONTACT DERMATITIS FROM BLACK RUBBER CHEMICALS

J.Roed-Petersen, O.J.Clemmensen, T.Menné and E.Larsen

Contact Dermatitis 18 (1988) 166-168

Black rubber chemicals are capable of causing an allergic contact dermatitis, in some cases associated with a purpuric capillaritis. A typical case of such a purpuric reaction is described in a man sensitive to black rubber chemicals.

MASS SPECTROMETRY OF UNDERIVATIZED 15-HYDROXYEICOSATETRAENOIC ACID AND 15-HYDROXYEICOSAPENTAENOIC ACID

Karsten Fogh, Knud Kragballe, Elfinn Larsen, Helge Egsgaard
and Vijai K.S.Shukla

Biomedical and Environmental Mass Spectrometry 17 (1988) 459-461

A direct mass spectrometric method for 15-hydroxy metabolites of arachidonic acid and of eicosapentaenoic acid is described. 15-Hydroxyeicosanoids have the capacity to inhibit the formation of leukotrienes, potent mediators of inflammation formed by the 5-lipoxygenase pathway of arachidonic acid metabolism and may therefore have anti-inflammatory properties. 15-Hydroxyeicosatetraenoic acid (15-HETE) and 15-hydroxyeicosapentaenoic acid (15-HEPE) were synthesized using soybean lipoxygenase and arachidonic acid and eicosapentaenoic acid as substrates. These hydroxy fatty acids were then purified by reversed-phase high-performance liquid chromatography. This modified procedure provides rapid synthesis of multimilligram quantities of 15-hydroxyeicosanoids for *in vitro* and *in vivo* studies. Electron impact mass spectra of 15-HETE and 15-HEPE could be obtained directly without derivatizations.

ISOMERIZATION OF THE DIMETHYL SULFOXIDE RADICAL CATION AND THE POSSIBLE ANALOGIES TO THE NEUTRAL SPECIES

Lars Carlsen and Helge Egsgaard

Journal of the American Chemical Society 110 (1988) 6701 - 6705

The interconvertibility of the dimethyl sulfoxide (DMSO) radical cation, its proton tautomeric *aci*-DMSO, and methyl methanesulfonate isomers, respectively, has been investigated by application of collision activation mass spectrometry and metastable ion studies. The isomerization reactions are discussed based on isotopic labeling studies as well as thermodynamical considerations. The interconvertibility of the radical cations of DMSO and *aci*-DMSO as well as the isomerization of the methyl methanesulfonate radical cation into the radical cation of DMSO could be concluded, whereas no unambiguous evidence concerning the possible operation of the DMSO to methyl methanesulfonate isomerization was obtained. Low-pressure gas-phase pyrolysis studies have been applied to elucidate the possible analogies to the corresponding neutral species.

LOW-PRESSURE AND HIGH-PRESSURE PYROLYSIS

Helge Egsgaard and Lars Carlsen

Thermochimica Acta 134 (1988) 321-326

Low-pressure and high-pressure pyrolyses of ethylene oxide and 1,2,3-oxadiazole are discussed. Pyrolyses at low pressures have been carried out applying the gas-phase Criegee-point pyrolysis technique and compared to available high-pressure data. The important interplay between quenching of reactive species and "hot" molecules, either by molecule-wall (low-pressure) or molecule-molecule (high-pressure) collisions, and collision free decompositions is discussed.

EXPERIMENTAL EVIDENCE FOR THE GASEOUS HSO_3 RADICAL. THE KEY INTERMEDIATE IN THE OXIDATION OF SO_2 IN THE ATMOSPHERE

Helge Egsgaard, Lars Carlsen, Helena Florencio, Thomas Drewello and
Helmut Schwarz

Chemical Physics Letters 148 No 6 (1988) 537-540

The HSO_3 radical has been generated and characterized by neutralization/reionization mass spectrometry. The HSO_3 radical exhibits a minimum lifetime of 0.7 μs when isolated in the gas phase. The principal unimolecular decomposition paths of HSO_3 were found to be loss of $\cdot\text{OH}$ and O , respectively.

UNIMOLECULAR DECOMPOSITION OF THE METHYL NITRITE RADICAL CATION. ON THE POSSIBLE OPERATION OF QUANTUM- MECHANICAL TUNNELING

Helge Egsgaard and Lars Carlsen

Chemical Physics Letters 147 No 1 (1988) 30-32

The mechanism for unimolecular fragmentation of the methyl nitrite radical cation, $\text{CH}_3\text{ONO}^{\cdot+}$, has been determined by mass spectrometric techniques applying deuterium and ^{18}O labelling. It could be unambiguously concluded that methyl nitrite radical cations possessing low internal energy fragment exclusively to the hydroxy-methyl cation. The recent proposal of a quantum-mechanical tunneling mechanism forcing an alternative reaction, leading to D_2NO^+ , on deuterium labelling of the methyl nitrite radical cation could unequivocally be excluded.

THE REACTION BETWEEN IMIDOGEN AND ELEMENTAL CARBON. AN ALTERNATIVE ROUTE TO INTERSTELLAR HCN ?

Lars Carlsen and Helge Egsgaard

J. Chem. Research (S), (1988) 118-119

The present paper describes the formation of HCN in a reaction between elemental carbon and imidogen, the latter being formed pyrolytically from azoimide.

In pyrolysis studies the importance of the nature of the hot surfaces is well known. Typically, certain reactions may be promoted due to the presence of hot reactive surfaces, as illustrated by, e.g., the apparent loss of atomic oxygen from compounds containing semi-polar X^+-O^- bonds ($\text{X} = \text{S}$ or N) upon pyrolysis on hot metal surfaces such as nickel, iron, or cobalt. In selected cases the surface may participate in the reaction upon delivery of additional atoms to reactive species in the gas phase producing thermodynamically stable products, as illustrated by studies of the gas-phase pyrolytic formation of benzonitrile from nitrobenzene and phenyl azide on hot carbon surfaces.

**IONIZATION ENERGIES AND THERMAL FRAGMENTATION
PATTERNS OF GASEOUS CYCLOPOLYARSANES AND-PHOSPHANES
 E_nR_n (E = As or P; R = Me, Bu^t, or CF₃; $n = 3-5$): A JOINT
TEMPERATURE-VARIABLE FIELD IONIZATION MASS SPECTROMETRIC
AND ULTRAVIOLET PHOTOELECTRON SPECTROSCOPIC
STUDY**

Susanne Elbel, Helge Egsgaard and Lars Carlsen

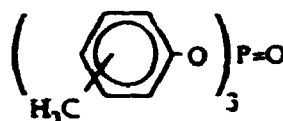
J. Chem. Soc. Dalton Trans. (1988) 195 - 200

Ultraviolet photoelectron spectroscopic (u.p.s.) data for gaseous As₃Bu^t₃, As₃(CF₃)₃, and As₃Me₃ are presented and discussed with respect to the known ionization potentials of the parent cyclopoly-phosphanes. Pyrolytically induced fragmentation patterns of representative cyclopoly-phosphanes and -arsanes in the gas phase have been analysed by high-temperature field ionization mass spectrometry (f.i.m.s.) and u.p.s. Evidence for a thermally generated transient phosphinidene P(CF₃) from [P(CF₃)₃]_n ($n = 4$ or 5) in the gaseous phase is provided by f.i.m.s., whereas products such as P₂ and CF₃ from secondary reactions are revealed by u.p.s. The u.p.s. upon thermal fragmentation of Sb(CF₃)₃ is also presented.

**TRICRESYLPHOSPHATE: OG HVAD ER SÅ DET ?
EN ARBEJDSHYGIEJNISK CASE-STORY SET FRA EN
ANALYTISK KEMISK SYNSVINKEL**

Lars Carlsen , Helge Egsgaard and Anders Feldthus

Dansk Kemi 69 (1988) 76 - 80



BIBLIOTEKET - FORSKNINGENS FUNDAMENT

Lars Carlsen

BIBLIOTEKER PÅ VOR VEJ, red. af N.-H. Gylstorff , T.Nielsen and M.Stockmarr
Bibliotekcentralens Forlag, Ballerup, (1988) 34 - 38

**PYROCATECHOL CONTACT ALLERGY FROM A PERMANENT
CREAM DYE FOR EYELASHES AND EYEBROWS**

Klaus E.Andersen and Lars Carlsen

Contact Dermatitis 18 (1988) 306 - 307

NEW FAST PREPARATION OF ^{123}I LABELLED RADIOPHARMACEUTICALS

J.Mertens, W.Vanryckeghem, M.Gyseman, J.Eersels, E.Finda-Panek and
L.Carlsen

European Journal of Nuclear Medicine 13 (1987) 380 - 381

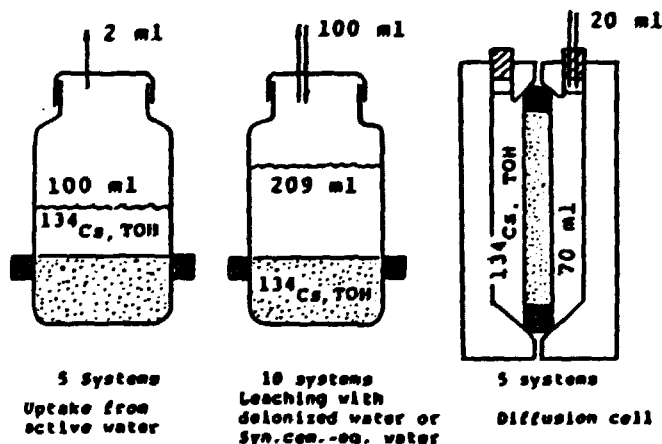
A new fast kit preparation of ^{123}I labelled radiopharmaceuticals such as IMP, HIPDM, MIBG and Hippuran is proposed. A radiochemical yield >99% is obtained at 100° C within 10-30 m.s. The new labelling procedure is based on the nucleophilic exchange in presence of Cu(I) and an excess of reducing agents. The four kit prepared ^{123}I -radiopharmaceuticals have been used with success in clinical studies involving 400 patients. The proposed method is also compared with earlier described methods which, yielding labelled side products and $^{123}\text{I}_2$, do not fulfill the requirements for kit labelling.

MECHANISMS AND INTERACTION PHENOMENA INFLUENCING RELEASE IN LOW- AND MEDIUM- LEVEL WASTE DISPOSAL SYSTEMS

Knud Brodersen and Karen Nilsson

Contract No: FI 1W - 0089 - DK - (B)

Progress report covering the period: 1/1 to 30/6 - 1988



HYGROSCOPIC WATER UPTAKE AND DRY/WET CYCLING COMPARED WITH NORMAL WATER EXPOSURE OF CEMENTED WASTE FORMS

K. Brodersen

**Twelfth International Symposium on the
Scientific Basis for Nuclear Waste Management**

October 10 - 13 (1988)

Internationales Congress Centrum, Berlin, Germany

Leaching as well as volume stability and the general structural behaviour of cemented waste (and also other waste forms) are dependent on the presence of water in the material and in the surroundings. Normally, conditioned waste materials are only tested for leaching, etc. under fully saturated conditions by immersion in water or solutions, but a direct contact with liquid water is not strictly necessary. A high humidity atmosphere has been found to be sufficient for water uptake or even considerable leaching to take place. Conditions of this type may appear in practice under inadequate intermediate storage conditions or after disposal in near surface repositories constructed in the unsaturated zone. Another feature, which for some materials appears to be of importance for the structural stability, is cyclic variations between water saturation and dry-out periods.

The phenomena have been investigated on a laboratory scale using simulated waste in form of cemented ion-exchange resins, sodium nitrate or sodium sulphate. Spherical samples have been found to be valuable for simultaneous determination of leaching diffusion coefficients for the major components, mainly sodium, and water uptake and swelling obtained from weight increase measurements for the samples in air and immersed in water.

The mechanisms involved are discussed and some possible consequences for practical waste management are mentioned.

The experimental work has been done under contract with the CEC.

DEGRADATION AND MATERIAL TRANSPORT FOR THIN PLATES OF CEMENT PASTES

Karen Nilsson and K. Brodersen

Twelfth International Symposium on the
Scientific Basis for Nuclear Waste Management

October 10 - 13, (1988)

Internationales Congress Centrum, Berlin, Germany

The thin-plate technique /1/ which is well suited for laboratory studies on cements, has been used in a series of equilibrium experiments aimed at studying material transport between concretes of different composition. The samples were cast from cement paste some of which contained excess silica fume, in the form of thin plates (4×1.5 cm) with a thickness between 0.3 mm and 2 mm. Part of the dry cement had earlier been activated in the OR3 reactor, and left for a cooling period of more than half a year after which the activity in the cement consisted mainly of ^{45}Ca . The thin plates were placed with a distance of 1 cm from each other in a small amount of water and after equilibration periods of up to two months at ambient temperature, the samples were weighed and analyzed for content of ^{45}Ca and of total calcium.

The extent of material transport is small under the conditions chosen but there appear to be a movement of calcium towards thin plates containing excess silica fume, where supposedly the pozzolanic reaction takes place. An aspect, which can of interest for crack-healing of cements.

Thin plates have also been employed in a study of the micro-structure of cements using the technique of SANS: Small Angle Neutron Scattering, which is a technique yielding information about structural features in the size range from 2 nm to about 100 nm. The purpose of the study is to investigate the effect of leaching of cements due to various corrosive conditions. The results obtained with samples of uncorroded cement paste are in agreement with findings by Allen et al /2/ and can be interpreted according to fractal theory. Extensive leaching of calcium from the cement plates, gave SANS results which did differed little from the results obtained from samples which had not been subjected to leaching. This may indicate that some features of the micro-structure are stable even after extensive chemical degradation. SANS results obtained on samples made by mixing moist silica fume and chemically pure calciumhydroxide indicates that the pozzolanic reaction gives rise to similar products as the hardening reactions in ordinary cements.

The experimental work has been carried out under contract with the CEC.

THE DECAY OF BENZO (*a*) PYRENE AND CYCLOPENTENO (*cd*) PYRENE IN THE ATMOSPHERE

Torben Nielsen

Atmospheric Environment 22 No.10 (1988) 2249 - 2254

The dominant source for PAH air pollution at Risø was Roskilde with 40,000 inhabitants situated 6 km south of the sampling site. Far distant sources of PAH were estimated to be insignificant. Benzo(*a*)pyrene and cyclopenteno(*cd*)pyrene were shown to decay in the atmosphere by means of the dependencies of the ratios of benzo(*a*)pyrene to benzo(*k*)pyrene and of cyclopenteno(*cd*)pyrene to chrysene + triphenylene on the wind direction and on the PAH pollution level. The decay appears to be relatively fast.

PAH I ATMOSFÆREN

Torben Nielsen

I "Forskerseminar om luftforureningsspredning,- deposition,
atmosfærekemi og - fysik" Forskningscenter Risø 16 - 17 November (1988)

COMPLEX FORMATION OF RADIONUCLIDES WITH ORGANIC LIGANDS COMMONLY FOUND IN GROUND WATER

Bror Skytte Jensen and Hanne Jensen

Radiochimica Acta 44/45 (1988) 45-49

The study of the formation of complexes under near natural conditions is discussed. Equations for the identification of mixed complexes and methods for determining their stability constants are derived. Examples of their application are given and possible consequences for geochemical computations are discussed.

GEOCHEMICAL MODELLING

B.Skytte Jensen and Hanne Jensen

Contract No. FI1W - 0079 - DK

Progress Report for the period 1/8 1986 to 1/8 1988

The objective of the project is to improve the previously developed geochemical computerprograms, the WHATIF series, by the introduction of new important equilibrium relations, by the improvement of the database and by the translation from the HP-basic language to one of the major languages i.e. PASCAL for use with a Personal Computer.

It is also considered important, that the final program shall be easy to use by the untrained user and that the program shall have a wide applicability both in the nuclear field as well as in other technological and scientific areas.

Much effort has been concentrated on organising the program- and data-structures and to develop "safe" algorithms such that the program will find the solution to almost any problem entered.

When new data are entered into the database conventional chemical formalism is used, thereby eliminating the need to assign and remember numbers for elements or species.

In addition algorithms for the handling of multielement ion-exchange and the formation of solid solutions has also been constructed and prepared for the introduction into the programs.

POLYMER COIL RELAXATION IN UNIAXIALLY ELONGATED POLY (ETHYLETHYLENE) OBSERVED BY SMALL-ANGLE NEUTRON SCATTERING

Kell Mortensen, Walther Batsberg, Ole Kramer and Lewis J.Fetters

**In: Biological and Synthetic Polymer Networks. Ed.By O. Kramer
From the 8th Polymer Networks Group Meeting held in Elsinore, Denmark
31 August - 5 September 1986
Elsevier Applied Science Publisher Ltd., England (1988) 369 - 382**

HIGH-VINYL POLYBUTADIENE CROSSLINKED IN THE STRAINED STATE TO DIFFERENT DEGREES OF CROSSLINKING

W.Batsberg, S.Hvidt, O.Kramer and L.J.Fetters

**In: Biological and Synthetic Polymer Networks. Ed.By O. Kramer
From the 8th Polymer Networks Group Meeting held in Elsinore, Denmark
31 August - 5 September 1986.
Elsevier Applied Science Publisher Ltd., England (1988) 509 - 516**

It is demonstrated that chain entangling in a well crosslinked polybutadiene gives distribution simply equal to the rubber plateau modulus of the uncrosslinked polymer which has a molecular weight of 2 million. It is found to be true for crosslink densities varying by as much as a factor of four. This result is obtained by introducing the crosslinks in the strained state. No theory and no assumptions are required.

QUANTITATIVE DETERMINATION OF CROSS-LINKING SITES IN BRANCHED POLYESTERS BY ^{13}C NMR SPECTROSCOPY

Søren Hvilsted

IUPAC 32nd International Symposium on Macromolecules.

Preprints, Kyoto, Japan (1988)

^{13}C -NMR ANALYSIS OF CROSSLINKING SITES IN BRANCHED POLYESTERS

Søren Hvilsted

In: Biological and Synthetic Polymer Networks. Ed. by O. Kramer

From the 8th Polymer Networks Group Meeting

held in Elsinore, Denmark 31 August - 5 September 1986.

Elsevier Applied Science Publishers Ltd., England (1988) 243-254

A detailed structural analysis of a four-component polyester based on adipic acid, isophthalic acid, neopentyl glycol (NPG) and trimethylol propane (TMP) is performed by ^{13}C -NMR spectroscopy. The ^{13}C resonances of the quaternary carbons of NPG and TMP are sensitive to all the possible different dicarboxylic acid combinations. All nine possible TMP polyester units are mimicked by synthesis of models with short well-defined adipic and/or isophthalic ester branches. The ^{13}C resonance of the quaternary TMP carbon in each model corresponds exactly to one of the nine different resonances in the quaternary TMP polyester multiplet. This enables an unequivocal identification of three fundamental kinds of TMP structures in the four-component polyester: the four different crosslinking sites, the three linear segments and the two end groups. The four ^{13}C resonances of the quaternary carbons of the crosslinking sites are evenly spaced by 0.4 ppm as a result of the stronger deshielding power of an isophthalate moiety when replacing the adipate analogue.

VISCOELASTICITY OF F-ACTIN AND F-ACTIN / GELSOLIN COMPLEXES

Paul A. Janmey, Søren Hvidt, Joyce Peetermans, Jennifer Lamb, John D. Ferry
and Thomas P. Stossel

Biochemistry 27 (1988) 8218 - 8227

Actin is the major protein of eukaryote peripheral cytoplasm where its mechanical effects could determine cell shape and motility. The mechanical properties of purified F-actin, whether it is a viscoelastic fluid or an elastic solid, have been a subject of controversy. Mainstream polymer theory predicts that filaments as long as those found in purified F-actin are so interpenetrated as to appear immobile in measurements over a reasonable time with available instrumentation and that the fluidity of F-actin could only be manifest if the filaments were shortened. We show that the static and dynamic elastic moduli below a critical degree of shear strain are much higher than previously reported, consistent with extreme interpenetration, but that higher strain or treatment with very low concentrations of the F-actin severing protein gelsolin greatly diminish the moduli and cause F-actin to exhibit rheologic behavior expected for independent semidilute rods, and defined by the dimensions of the filaments, including shear rate independent viscosity below a critical shear rate. The findings show that shortening of actin filaments sufficiently to permit reasonable measurements brings out their viscoelastic fluid properties. Since gelsolin shortens F-actin, it is likely that the effect of high strain is also to fragment a population of long actin filaments. We confirmed recent findings that the viscosity of F-actin is inversely proportional to the shear rate, consistent with an indeterminate fluid, but found that gelsolin abolishes this unusual shear rate dependence, indicating that it results from filament disruption during the viscosity measurements. The viscosity of gelsolin/F-actin complexes at very low shear rates is proportional to approximately the fifth power of the filament length. Therefore, proteins that control actin filament length can powerfully regulate the rheologic behavior of cytoplasmic actin.

UV SPECTRUM AND KINETICS OF HYDROXYMETHYL RADICALS

Palle Pagsberg, Jette Munk, Alfred Sillesen and Christopher Anastasi

Chemical Physics Letters 146 No 5 (1988) 375-381

Hydroxymethyl radicals were produced by pulse radiolysis of gas mixtures with varying mole ratios of Ar, SF₆, HCl and CH₃OH to initiate the reactions (1) X + CH₃OH → HX + CH₂OH and (2) X + CH₃OH → HX + CH₂O, where X = OH, F and Cl. The ultra-violet absorption spectrum of CH₂OH is composed of several vibronic progressions in the range 200–285.3 nm. Band heads of 3s and 3p Rydberg transitions have been identified by comparison with the results of recent ab initio configuration interaction studies of CH₂OH. Variations in the yields and kinetics of CH₂OH were studied by monitoring the transient absorption at the 0–0 band of the 3s Rydberg transition at 285.3 nm. Branching ratios for reactions (1) and (2) with X = F and OH were determined as well as rate constants for a number of elementary reactions, including the self-reaction of CH₂OH and the reaction with O₂.

AB INITIO CONFIGURATION INTERACTION STUDY OF THE RYDBERG STATES OF THE HYDROXYMETHYL RADICAL CH₂OH

Sten Rettrup, Palle Pagsberg and Christopher Anastasi

Chemical Physics 122 (1988) 45-51

The ultraviolet absorption spectrum of the hydroxymethyl radical has been studied by ab initio configuration interaction methods using a large Gaussian-type basis set. The first four vertical electronic transition energies have been calculated to be at 287, 243, 221 and 219 nm. Dipole moments are presented for all the states together with the oscillator strengths for the transitions. A detailed analysis of the orbitals shows that the transitions are of Rydberg type which can be classified as $\pi \rightarrow 3s$, $\pi \rightarrow 3p_x$, $\pi \rightarrow 3p_y$ and $\pi \rightarrow 3p_z$

**GAS PHASE KINETICS OF FREE RADICALS STUDIED BY PULSE
RADIOLYSIS COMBINED WITH TIME-RESOLVED INFRARED
DIODE LASER SPECTROSCOPY**

Palle Pagsberg, Emil Ratajczak and Alfred Sillesen

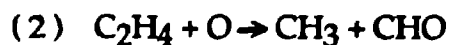
The Laser Analytics Letter 10 September (1988) 1-4

**KINETICS OF METHYL RADICALS STUDIED BY PULSE RADIOLYSIS
COMBINED WITH INFRARED DIODE LASER SPECTROSCOPY**

Palle Pagsberg, Emil Ratajczak and Alfred Sillesen

Kinetics and Mechanisms of Elementary Chemical Processes of
Importance in Combustion. Contract No. EN3E - 0095 - DK (B)
For the period April - December 1988

Rate coefficients at $T = 300 \text{ K}$ for the reactions



KINETICS AND MECHANISMS OF ELEMENTARY CHEMICAL
PROCESSES OF IMPORTANCE IN COMBUSTION

Jette Munk, Palle Pagsberg, Emil Ratajczak, Barbara Sztuba and Alfred Sillesen

Risø - M - 2688 January 1988

SPECTROKINETIC STUDIES OF THE REACTION OH + CO

Jette Munk, Palle Pagsberg, Knud Sehested and Alfred Sillesen

Contract No. EN3E - 0095 - DK (B)

For the period October 1987 - April 1988

Low-pressure Channel: $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$

High-pressure Channel: $\text{CO} + \text{OH} + \text{M} \rightarrow \text{COOH} + \text{M}$

**TROPOSPHERIC NO_x CHEMISTRY -
GAS PHASE AND MULTIPHASE ASPECTS**

Air Pollution Research Report 9

**Proceedings of a Workshop organised within the framework of Working Party 2
"Chemical and Photochemical Reactions" of the Concerted Action
"Physico - Chemical Behaviour of Atmospheric Pollutants",
COST 611, held at Risø National Laboratory, Roskilde, 17 - 18 September 1987
Report EUR 11440**

Ed. by O.J.Nielsen and R.A.Cox

**SPEKTROKINETIC STUDIES OF NO₃ . SOURCE REACTIONS,
SELFREACTIONS, AND REACTIONS WITH ORGANIC COMPOUNDS**

**Kirsten Eriksen, Christian Lohse, Ole John Nielsen, Palle Pagsberg,
Emil Ratajezak and Alfred Sillesen**

In: Tropospheric NO_x Chemistry - Gas Phase and Multiphase Aspects

Ed. by O.J.Nielsen and R.A.Cox, EUR 11440, 128 - 129

SPECTROKINETIC STUDIES OF NO₃ REACTIONS WITH CH₃ AND Cl

Palle Pagsberg, Emil Ratajczak, Alfred Sillesen and Anders Lund

In: Tropospheric NO_x Chemistry - Gas Phase and Multiphase Aspects

Ed. by O.J.Nielsen and R.A.Cox, EUR 11440, 130 - 132

**SPECTROKINETIC STUDIES OF NO₃ - SOURCE REACTIONS,
SELF - REACTION AND REACTIONS WITH SELECTED ALKENES**

K.Eriksen, C.Lohse, O.J.Nielsen, P.Pagsberg, A.Sillesen and E.Ratajczak

SPECTROKINETIC STUDIES OF NO₃ REACTIONS WITH CH₃ AND Cl

P.Pagsberg, E.Ratajczak, A.Sillesen and A.Lund

both in:

TROPOSPHERIC NO_x CHEMISTRY - GAS PHASE AND MULTIPHASE ASPECTS

Ed: O.J.Nielsen and R.A.Cox

**Proceedings of the 6th workshop organised within the framework of the Working
Party 2 "Chemical and Photochemical Reactions" of the Concerted Action
"Physico - Chemical Behaviour of Atmospheric Pollutants" held at Risø National
Laboratory, Roskilde, 17 - 18 September 1987
Risø - M - 2630**

ATMOSPHERIC CHEMISTRY OF ORGANIC SULFUR AND NITROGEN COMPOUNDS

Ole John Nielsen, Howard W. Sidebottom and Jack J. Treacy

First Annual Progress Report 1988 (EV4V - 0067 - C9)

Rise - M - 2755 (1988)

The work carried out during the first year of a four year Danish-Irish contract with the European Economic Community is described. The reactions of OH radicals with dialkyl sulfides and nitroalkanes have been studied applying both an absolute technique of pulse radiolysis with kinetic spectroscopy and a relative rate method using conventional smog chamber facilities. The reactions of OH with dimethyl sulfide and nitromethane have been investigated in special detail. Rate constants for reaction of Cl atoms with the same compounds have been determined using the relative rate method.

ABSOLUTE AND RELATIVE RATE CONSTANTS FOR THE GAS-PHASE REACTION OF OH RADICALS WITH NITROALKANES AT 295 K AND 1 ATM

Ole John Nielsen, Howard W. Sidebottom, Denis J. O'Farrell, Michael Donlon
and Jack Treacy

In: MECHANISMS OF GAS PHASE AND LIQUID PHASE CHEMICAL
TRANSFORMATIONS IN TROPOSPHERIC CHEMISTRY Ed. by R. A. Cox
A joint COST-EUROTAC meeting held at the School of Chemical Sciences,
University of East Anglia, NORWICH NR4 7TJ England, 20-22 September 1988

ABSOLUTE AND RELATIVE RATE CONSTANTS FOR THE GAS-PHASE
REACTION OF OH RADICALS WITH CH_3NO_2 , CD_3NO_2
AND $\text{CH}_3\text{CH}_2\text{CH}_3$ AT 295 K AND 1 ATM

Ole J.Nielsen, Howard W.Sidebottom, Denis J.O'Farrell, Michael Donlon
and Jack Treacy

Chemical Physics Letters 146 (1988) 197 - 203

The rate constants for the gas - phase reaction of OH radicals with nitromethane, deuterio-nitromethane and propane have been determined at 295 ± 2 K and a total pressure of approximately 1 atm; a photolytic relative technique and an absolute method were applied. Methyl nitrite was used as the OH source in the relative method. In the absolute technique, pulse radiolysis was combined with kinetic spectroscopy. H_2O - Ar mixtures were irradiated and the OH kinetics recorded by following the transient light absorption around 309 nm. The results are compared with literature data.

**RESONANCE RAMAN SPECTRA OF HEXATRIENE MODEL
POLYENES IN GROUND AND EXCITED TRIPLET STATES**

R.Wilbrandt, F.W.Langkilde, A.M.Brouwer and H.J.C.Jacobs

**In: SPECTROSCOPY OF BIOLOGICAL MOLECULES, NEW ADVANCES,
Ed. by E.D.Schmidt, F.W.Schneider and F.Siebert, Wiley, (1988) 279 - 284**

**MODEL POLYENES: THEORETICAL AND EXPERIMENTAL
RESONANCE RAMAN STUDIES OF THE LOWEST TRIPLET
STATE OF DEUTERATED AND PARENT HEXATRIENES**

R.Wilbrandt, F.W.Langkilde, A.M.Brouwer, F.Negri and G.Orlandi

**In: Proc. XI Int. Conf. Raman Spectrosc. Ed. by R.J.H.Clark and D.A.Long
Wiley (1988) 611 - 612**

A NEW RADIOCHROMIC THIN-FILM DOSIMETER SYSTEM

A. Miller, W. Batsberg and W. Karman

Radiat. Phys. Chem. 31 Nos 4-6 (1988) 491 - 496

A film dosimeter based on pararosaniline cyanide dissolved in polyvinyl butyral (PVB) has been developed and its properties are described. The dosimeter is made in 3 versions: 1) a clear, thin film that requires a thickness measurement for evaluation, 2) a film with a relatively high absorbance for automatic thickness correction, 3) a UV-protected pressure-sensitive adhesive tape. The response of the dosimeter is independent on the dose rate, and it may be used for routine dose measurement of both gamma and electron irradiation. Its high spatial resolution makes it particularly useful for dose distribution measurements.

DOSIMETRY FOR INDUSTRIAL ELECTRON BEAM IRRADIATION

Arne Miller

IAEA Technical Contract 4748/TC

Report for the period 1 August 1987 - 31 July 1988

APPROVAL AND CONTROL OF RADIATION PROCESSES, EB AND GAMMA

Arne Miller

Radiat. Phys. Chem. 31 Nos 1-3 (1988) 385 - 393

The documentation which is needed for approval of radiation treated products includes a facility description and an initial plant commissioning procedure. The description of the facility must put particular emphasis on those parameters, which in effect determines the dose in the product. For a gamma plant these are source strength and geometry, product conveyor geometry and mode of transport, and in a similar manner for electron accelerator plants, the beam characteristics, power and geometry, and product transport parameters.

The initial commissioning concerns measurement of dose and dose distribution in a reference product, and of procedures, which describe how traceability of these measurements to primary standards is obtained. Commissioning measurements must be repeated whenever major changes of the facility are made.

In order to maintain the correct dose, a routine monitoring system must be established. This consists of measurement and recording of the process parameters, and of routine dosimetry. For a gamma plant, the most important (and sometimes the only) variable parameter is the product speed (or dwell time), while for electron beam plants, the beam parameters must also be recorded.

For approval of individual processes or products, it is necessary to demonstrate that the dose within the actual product is within the process design limits. Measurement of dose distribution is therefore needed in order to locate minimum and maximum dose points, and subsequently it is needed to determine the variability of dose at these points.

DOSE DISTRIBUTIONS AND DOSE LIMITS IN FOOD IRRADIATION

A.Miller

In: Health Impact, Identification and Dosimetry of Irradiated Foods.
WHO Working Group on Health Impact and Control Methods of Irradiated Foods,
Neuherberg, 17- 21 Nov. 1986
Ed. by K.W. Bögl, Dieter F. Regulla and Michael J. Suess
Institut für Strahlen Hygiene des Bundesgesundheitsamtes, Neuherberg (1988)
ISH-Heft. 125 405 - 414

REACTIVITY OF H, OH AND e_{aq}^- WITH NICOTINIC ACID: A PULSE RADIOLYSIS STUDY

S.Solar, W.Solar, N.Getoff, J.Holcman and K.Sehested

Radiat. Phys. Chem. 32 No 3 (1988) 585 - 592

The reactivity of aqueous nicotinic acid (NA) towards OH, e_{aq}^- and H-atoms has been investigated in the pH-range 0.3–13.8. The OH attack on NA [$k = (2.5 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$] and its *N*-protonated forms [$k = (2.2 \pm 0.2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$] gives OH-adducts with pH-dependent optical spectra [$\text{NC}_5\text{H}_4(\text{OH})\text{COO}^-$: $\lambda_{\text{max}} = 310 \text{ nm}$, $\epsilon_{310} = 1800 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$; $^-\text{HNC}_5\text{H}_4(\text{OH})\text{COO}^-$: $\lambda_{\text{max}} = 325 \text{ nm}$, $\epsilon_{325} = 2000 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$]. $\text{pK}_a = 4.5 \pm 0.2$ was determined for these two transients. The reaction of H-atoms with NA in the pH-range 6–12 [$k = (6.0 \pm 0.5) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$] results in the formation of one type of transient, the H-adducts on ring carbons ($\lambda_{\text{max}} = 315 \text{ nm}$, $\epsilon_{315} = 4500 \pm 200 \text{ M}^{-1} \text{ s}^{-1}$; $\text{pK} = 6.7 \pm 0.2$). With the *N*-protonated forms of NA, however, two kinds of radicals are produced: pyridinyl ($\lambda_{\text{max}} = 285 \text{ nm}$, $\epsilon_{285} = 7800 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$; $\lambda_{\text{max}} = 410 \text{ nm}$, $\epsilon_{410} = 3100 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$) and H-adduct on ring carbons ($\lambda_{\text{max}} = 340 \text{ nm}$, $\epsilon_{340} = 4600 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$). The reaction of e_{aq}^- with NA was reinvestigated. The kinetic and spectroscopic data are in good agreement with those previously reported.

HO₂ AND O₂⁻ RADICALS AT ELEVATED TEMPERATURES

Hilbert Christensen and Knud Sehested

The Journal of Physical Chemistry, 92 No 10 (1988) 3007 - 3011

The spectra of HO₂ and O₂⁻ radicals were determined in the temperature range 20–300 °C in aqueous solutions with 0.2-MPa oxygen and about 10-MPa hydrogen pressure. In this temperature range the wavelengths at maximum absorption and the half-widths of the spectra change very little. The relative temperature coefficient of $\epsilon_{\text{max}}G$ is 0.15 and 0.25% K⁻¹ for HO₂ and O₂⁻, respectively. In the temperature range 20–100 °C the change in pK_a is small, but above 100 °C pK_a increases with an increasing rate up to a value of 6.15 (molal unit) at 285 °C. In acid solution, pH ≤ 2, the bimolecular decay rate constant for HO₂ has an activation energy of 20.6 kJ mol⁻¹ (4.9 kcal mol⁻¹). At higher pH the decay is caused by the reaction between HO₂ and O₂⁻. This reaction follows the Arrhenius parameters up to 100 °C with an activation energy of 7.6 kJ mol⁻¹ (1.8 kcal mol⁻¹). Above 100 °C the decay rate increases drastically. At higher temperatures (≥ 200 °C) a reaction with an activation energy of $80 \pm 12 \text{ kJ mol}^{-1}$ ($19 \pm 3 \text{ kcal mol}^{-1}$) becomes rate determining. This reaction is tentatively ascribed to the equilibrium reaction $\text{O}_2^{\cdot-} + \text{O}_2^{\cdot-} \rightleftharpoons \text{O}_4^{2-}$ followed by $\text{H}^+ + \text{O}_4^{2-} \rightarrow \text{HO}_2^{\cdot-} + \text{O}_2$. The mechanism may involve the unstable intermediate HO₄⁻. The high activation energy is ascribed to the forward reaction in the equilibrium which makes this reaction negligible at lower temperatures.

RADIOLYSIS OF REACTOR WATER

Hilbert Christensen, Bertil Persson and Knud Sehested

In: 1988 JAIF International Conference on Water Chemistry in Nuclear Power Plants

Vol. 2 Tokyo, 19 - 22 Apr. 1988

Japan Atomic Industrial Forum, Tokyo (1988) 505 - 510

In connection with the introduction of HWC it has become of great interest to predict the concentrations of radiolytic species at various points in a BWR. Computer modelling, using a chemical kinetics program, has been carried out to simulate the radiolysis of high-temperature water, such as the reactor coolant. The effect of changes in parameters, such as rate constants, G-values, impurities and mechanisms, has been studied systematically in order to obtain the best agreement between measured and calculated results. Recent measurements in the down-comer of the Forsmark-2 reactor both during NWC and HWC have been used for this comparison. A deviation of the down-comer in regions with varying dose rates, assuming a laminar flow, improves the correlation between measured and calculated concentrations. In order to improve the reliability of the calculations rate constant have been determined at high temperatures for some important reactions. The technique used in these determinations and some recent results will be described. The calculations have pointed out some additional important reactions, for which it is planned to determine the rate constants in future investigations.

CALCULATION OF ALPHA -RADIOLYSIS OF AQUEOUS SOLUTIONS
INCLUDING DIFFUSION OF THE PRODUCTS THROUGH
A GLASS FILTER

H.Christensen and E.Bjergbakke

Studsvik Report NS - 88 - 299 (1988)

Calculations of α -radiolysis of aqueous solutions at a dose rate of 73 rad/s have been carried out. The amounts of hydrogen, oxygen and hydrogen peroxide which diffuse through a glass filter have been calculated using the program CHEMSIMUL.

Calculated yields of H_2O_2 (~1.05) are in fair agreement with experimental yields (~1.10) for "pure" water, pH 8, (case 1a) and aqueous methanol solutions, pH 5, (case 2). The decrease in measured yields found in the experiments including hydrocarbonate solutions (cases 1b and 1c, $G(H_2O_2) = 0.8$) was not found in the calculations ($G(H_2O_2) = 1.0$). The agreement in calculated and measured concentrations of Fe^{2+} in solutions initially containing $1.8 \mu M Fe^{2+}$ (case 1d) is fair, considering the likelihood of a reaction between Fe^{2+} and oxygen.

STRÅLINGSFYSIK OG DOSIMETRI

J.W.Hansen and K.J.Olsen

**Til: Dansk Forening for Medicinsk Fysik
Årsrapport 1987**

DECAY IN RADICAL CONCENTRATION IN AN AMINO ACID FOLLOWING HEAVY CHARGED PARTICLE EXPOSURES

J.W.Hansen and K.J.Olsen

**GSI Scientific Report 1987 ISSN 0174 - 0814 March (1988) 218
Gesellschaft für Schwerionenforschung mbH, Darmstadt**

**POSTAL DOSIMETRY COMPARISONS WITH ALANINE
DOSIMETERS**

K.J.Olsen and J.W.Hansen

**Physics in Medicine and Biology, Vol 33, 99
Proceedings of the World Congress on Medical Physics and Biomedical Engineering
6 - 12 August (1988) San Antonio, Texas**

**PREDICTING DECAY IN RADICAL CONCENTRATION IN AN AMINO
ACID FOLLOWING HEAVY ION EXPOSURES**

J.W.Hansen and K.J.Olsen

**Physics in Medicine and Biology, Vol 33 , 28
Proceedings of the World Congress on Medical Physics and Biomedical Engineering
6 - 12 August (1988) San Antonio, Texas**

DETERMINATION OF IONIZATION CHAMBER KERMA CORRECTION FACTORS FOR MEASUREMENTS IN MEDIA EXPOSED TO ORTHOVOLTAGE X-RAYS

M.Kristensen, P.Hjortenberg, J.W.Hansen and M.Wille

DOSIMETRY IN RADIOTHERAPY, Vol 1, 149 - 174

Proceedings of an International Symposium on Dosimetry in Radiotherapy

International Atomic Energy Agency

31 August - 4 September 1987, Vienna

Kerma correction factors, α_K , were determined for a cylindrical Farmer chamber and for two spherical chambers, having air-equivalent walls and diameters of 19 and 10 mm, respectively. The chambers were irradiated at a depth of 2 cm in water with two X-ray beams, having a HVT of 2.3 mm Al and 4.6 mm Al, respectively. α_K is defined according to $M_u = M_u \cdot N_K \cdot \alpha_K$. α_K is calculated for the spherical chambers assuming that the chamber signal is proportional to the mean value of kerma averaged over a spherical surface concentric with the wall. Three experimental determinations of α_K were made using three different types of detectors: (a) an ionization chamber, (b) LiF, and (c) alanine. The detectors had volumes less than 15 mm³. Experimental values of α_K from 0.9 to 1.0 were obtained. Calculated and experimental values show agreement within 4%. In agreement with the recommendation of ICRU over the past 25 years values close to unity were obtained for the Farmer chamber. Recently it has been recommended that absorbed dose to water be derived from absorbed dose to graphite. Using this method, chambers similar to those investigated here have been calibrated at similar X-ray qualities. Values of α_K thus obtained were approximately 15% higher than those obtained by the authors. It is suggested that this discrepancy could be caused by errors in the theoretical values of $(\mu_{en}/\rho)_{\text{carbon}}^{\text{air}}$.

**ON THE DOSE-RESPONSE RELATIONSHIPS FOLLOWING THE
IRRADIATION OF AMINO ACIDS**

K.J.Olsen and J.W.Hansen

Radiation Research 116, (1988) 547 - 549

**EXPERIMENTAL AND THEORETICAL INVESTIGATIONS OF THE
ALANINE DOSIMETER AS A PERSONAL ACCIDENT DOSIMETER
IN MIXED FIELD RADIATION**

Johnny W.Hansen , K.Sehested and Kjeld J.Olsen

Radiation Protection Programme. Progress Report 1987

Brussels (1988) 101 - 106 EUR - 11464

A POLYMER- ALANINE FILM FOR MEASUREMENTS OF RADIATION DOSE DISTRIBUTIONS

J.Janovsky', J.W.Hansen and P.Černoch

Appl. Radiat. Isot. 39 No 7 (1988) 651 - 657

Int. J. Radiat. Appl. Instrum. Part A

A film dosimeter (0.35 mm thick) composed of polyethylene-vinyl acetate and microcrystalline L-x-alanine has been prepared and investigated with respect to dosimetric properties using electron spin resonance spectroscopy. The useful absorbed dose range is ~ 25 to 10^5 Gy and no dose-rate dependence of the response is observed between 1 and 10^7 Gy s^{-1} within the dose range up to 50 kGy. With irradiation temperature increasing from 25 to 80°C, the response increases at most by 10%. The response is stable, within experimental uncertainty, at least up to 2500 h after irradiation. The suitability of the polymer-alanine film for measurements of ionizing photon and electron dose distributions is demonstrated.

TEORETISKE OG EKSPERIMENTELLE UNDERSØGELSER
AF ASBESTS NEDBRYDELIGHED

Anne Belinda Bjerre, Bror Skytte Jensen and Emil Sørensen

Kemiafdelingen. Report 35903 - 68 - 83 / hk Maj 1988

VÅDOXIDATION SAMT EKSTRAKTION AF METALLER
UNDER HØJT TRYK OG HØJ TEMPERATUR

Emil Sørensen, Anne Belinda Bjerre and Jørgen Jensen

Proceskemi. Forsøgsrapport 35957 - 68 - 85 - 1 / hk (1988)

RECOVERY OF GOLD FROM A GOLD-THIOUREA LOADED ION-EXCHANGER

E.Sørensen and A.B.Bjerre

Proceedings of the First International Conference on Hydrometallurgi (ICHM' 88)

Beijing, 12 - 15 October 1988

Ed: Zheng Yulian, Xu Jiazhong , Beijing 1988, 517 - 520

The use of a strong acid cation-exchanger for the recovery of gold from a thiourea leach solution was investigated. It is well-known that the gold-thiourea complex is readily absorbed on a cation-exchanger. The problems lie in the purification and elution of the gold so as to fully regenerate the ion-exchanger. The most common impurities are copper and iron, which are stripped by $\text{HNO}_3 + \text{H}_2\text{O}_2$ and by NH_4NO_3 respectively.

The gold-thiourea complex is retained very firmly by the ion-exchanger and refuses to be displaced by other ions. The desorption is therefore brought about by a ligand-exchange process using thiosulphate, which yields the complex anion AuS_2O_3^- . Since the ion-exchanger has no affinity to anions the AuS_2O_3^- will leave the column immediately. It is important for successful elution that pH is kept within 5-6.5. Ammonium thiosulphate is the preferred reagent.

Gold is recovered from the eluate by reduction with aluminium.

It has been established that the ion-exchanger preserved its capacity unchanged for reloading with gold from a thiourea leach solution.

THE USE OF MOSS ANALYSIS FOR MEASURING ATMOSPHERIC HEAVY METAL DEPOSITION IN THE NORDIC COUNTRIES

K.Pilegaard, L.Rasmussen and Å. Rühling

In: Pollution Climates in Europe And their Perception by Terrestrial Ecosystems
Proceedings of a Workshop. Liebefeld - Bern, 27-30 April 1987, EUR 11432, 192 - 200

The atmospheric heavy metal deposition as reflected in the concentrations in moss was monitored in a joint Nordic project in Denmark, Finland, Norway and Sweden in 1985. The aims of the project were to assess the regional and temporal variation in the atmospheric deposition of As, Cd, Cr, Cu, Fe, Pb, Ni, V and Zn. In this short presentation the background for the study, the methods and examples of the results are given. For all the metals the concentrations are higher in the southern part of Scandinavia than in the northern part. Some local emission sources were found to be important on the regional scale. Comparisons with similar investigations in Sweden every 5th year since the late 1960s showed a marked reduction during the period.

ATMOSPHERIC HEAVY METAL DEPOSITION IN NORTHERN EUROPE MEASURED BY MOSS ANALYSIS

L.Rasmussen, K.Pilegaard and Å.Rühling

In: AIR POLLUTION AND ECOSYSTEMS

Proceedings of an International Symposium held in Grenoble, France,

18 - 22 May 1987, Ed: P.Mathy

D.Reidel Publ. Company (1988) 560 - 565

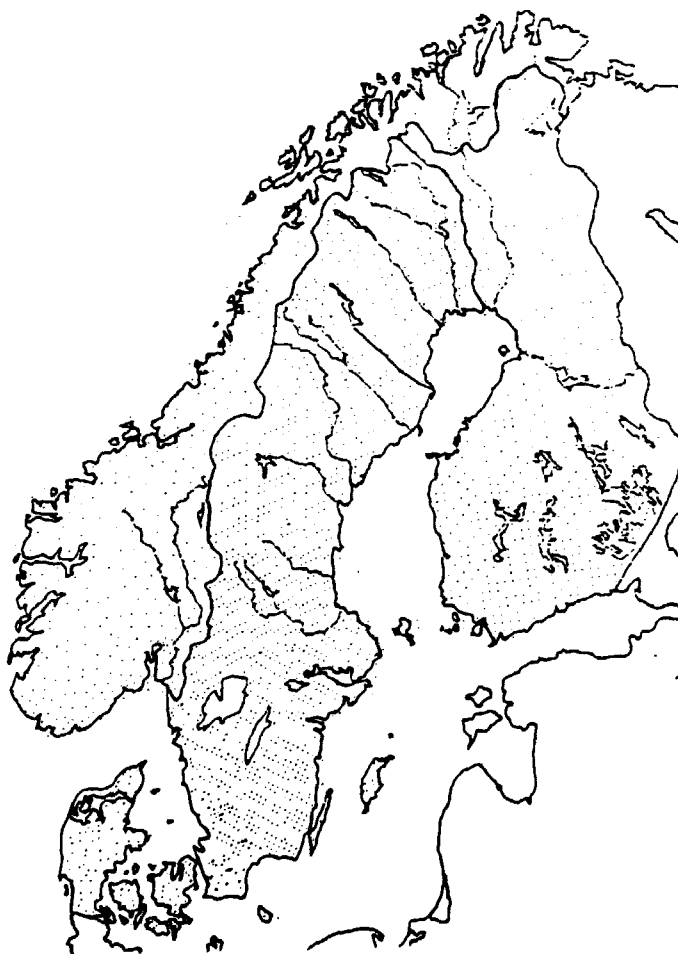


Fig. 1. Location of sampling sites.

LECTURES AND POSTERS

- 1.1 K. Heydorn: "Research Reactors - Tools for the Future". Symposium - 25 jaar HOR, Delft, 11th May 1988.
- 1.2 K. Heydorn: "Radiochemical Methods for Selenium in Biological Materials", American Nuclear Society 1988 Annual Meeting, San Diego, 14th May 1988.
- 1.3 K. Heydorn: "Ancient Mesopotamian Ceramics". 1st Scandinavian Symposium on Chemometrics, Lappeenranta, 7th Oct. 1988.
- 1.4 K. Heydorn: "Intern og extern laboratoriekontrol". AMI Formidlingsmøde, Arbejds miljøinstituttet, 2nd Dec. 1988.
- 2.1 Per Solgaard: "ICP/MS: A new promising tool in inorganic analysis. CEN Cadarache, Frankrig, 20th October 1988.
- 2.2 Lis Vinther Kristensen, Elfinn Larsen og Per Solgaard: "ICP/MS: Måling af Pb isotopforhold". Dansk Selskab for Massespektrometri, Odense Universitet, 28th January 1988.
- 2.3 Lis Vinther Kristensen, Elfinn Larsen and Per Solgaard: "ICP/MS: Measurement of Nickel." 11th Int. Mass Spec. Conf., Bordeaux, Aug /Sep 1988.
- 2.4 Gustav Bojesen, Elfinn Larsen and Vijai K.S. Shukla: "Collision Activation of Glucosinolate Anions" 11th Int. Mass Spec. Conf., Bordeaux, Aug/Sep 1988.
- 2.5 Helge Egsgaard and Lars Carlsen: "Low-pressure and high-pressure pyrolysis". The 9th Int. Congress on Thermal Analysis, Jerusalem, Israel, 21-25th August.
- 2.6 Helge Egsgaard and Lars Carlsen: "Unimolecular and Collision Induced Decomposition of Protonated Carbonic Acid". 11th International Mass Spectrometer Conference, Bordeaux, 29th Aug-2nd Sep.1988.
- 2.7 T. Drewello, C.B. Lebrilla, H. Florencio, L.Carlsen, H. Egsgaard and H. Schwarz: "NRMS-The bridge to the chemistry of neutral reactive intermediates". 11th International Mass Spectrometry Conference, Bordeaux, 29th Aug-2nd Sep.1988.
- 2.8 Helge Egsgaard and Lars Carlsen: "The fate of molecules in low-pressure pyrolysis reactors". Contribution to meeting in Dansk Selskab for Massespektrometri, Odense, Jan. 1988.
- 2.9 Asger B. Hansen: "Experimental Characterization of Petroleum Fractions: DAN-PRISE introduction,

Norsk Hydro's Forskningscenter, Bergen, 11th October 1988.

2.10 Asger B. Hansen: "Hydrocarbon Characterization at the Chemistry Department, Risø". DAN-PRISE introduction, DANOP, DONG and DOPAS, Hørsholm, 24th November 1988.

3.1 Helge Egsgaard and Lars Carlsen: "Interconvertability of DMSO-, aci-DMSO-, and methylmethanesulfenate radical cations". Contribution to meeting in Dansk Selskab for Massespektrometri, Odense, Jan. 1988.

3.2 Lars Carlsen: "Anvendelse af MS, MS/MS, MS/MS/MS til studier af gasfase reaktioner". Invited lecture at meeting in Dansk Selskab for Massespektrometri, Odense, Jan. 1988.

3.3 Lars Carlsen: "Risø R&D Activities in the field of environmental pollution". Contribution to IAEA Research co-ordination meeting on Nuclear Techniques in the study of pollutant transport in the environment: Interaction of solutes with geological media (methodological aspects). Rio de Janeiro, Febr. 1988.

3.4 Lars Carlsen: "The application of column chromatography in the assessment of pollutant transport in the environment". Invited lecture at IAEA Research co-ordination meeting on Nuclear Techniques in the study of pollutant transport in the environment: Interaction of solutes with geological media (methodological aspects). Rio de Janeiro, Febr. 1988.

3.5 Lars Carlsen, Anders Feldthus and Peter Bo: "An approach to solid state kinetics". Contribution to 8th International Symposium on Analytical and Applied Pyrolysis (Pyrolysis 88), Lund, June 1988.

3.6 Lars Carlsen: "Activation parameters for hydrocarbon formation. An approach to solid state kinetics". Lecture at the IEA-CCS meeting at Risø, Sept. 1988.

3.7 Lars Carlsen: "Application of mass spectrometric techniques in the study of gas-phase reactions". Invited lecture at 8. Forschungsklausurtagung über Synthese, Strukturuntersuchungen und Struktur-Wirkungs-Beziehungen von Organischen Verbindungen (Vorrangig S-Verbindungen, Lähnwitz (Pädagogische Hochschule "Liselotte Herrmann" Güstrow), DDR, Okt. 1988.

3.8 Lars Carlsen: "Application of mass spectrometric techniques in the study of gas-phase reactions". Lecture at Wilhelm-Pieck-Universität Rostock, DDR, Okt. 1988.

3.9 Torben Nielsen: "Forekomster af kræftfremkaldende PAH i luften i København". Møde om "Luftforureningen i Danmark - niveauer, sundhedsskader, kilder, begrænsning", Dansk Selskab for Miljøkemi, H.C. Ørsted Institutet, 13th Oktober 1988.

3.10 Torben Nielsen: "PAH i atmosfæren". Forskerseminar om luftforureningsspredning, -deposition, atmosfærekemi og -fysik. Forskningscenter Risø, 16-17th November 1988.

3.11 K. Brodersen: "Hygroscopic Water Uptake compared with normal Water Exposure of Cemented Waste Forms". Twelfth Int. Symp. on the Scientific Basis for Nuclear Waste Management, Berlin, FRG 10-13th Oct. 1988.

3.12 Karen Nilsson and K. Brodersen: Degradation and Material Transport for thin Plates of Cement Pastes. Twelfth Int. Symp. on the Scientific Basis for Nuclear Waste Management, Berlin, FRG 10-13th Oct. 1988.

4.1 Kristoffer Almdal: "SEC-Bestemmelse af polymerers molekylvægtsfordeling i blandede opløsningsmidler". Nordiska Polymerdagar 1988 i Göteborg, 24-25th August 1988.

4.2 S. Hvilsted: "Determination of Structural Units in Saturated Multicomponent Polyesters by Quantitative ^{13}C NMR Spectroscopy". Istituto Guido Donegani, Novara, Italy, 20th June 1988.

4.3 S. Hvilsted: "Structural Elucidation of Saturated Multicomponent Polyesters by Quantitative ^{13}C NMR Analysis". Dipartimento di Ingegneria Chimica, Università di Pisa, Italy, 22nd June 1988.

4.4 S. Hvilsted: "Quantitative Determination of Cross-Linking Sites Branched Polyesters by ^{13}C NMR Spectroscopy". IUPAC 32nd International Symposium on Macromolecules (MACRO 88), Kyoto, Japan, 5-6th August 1988.

5.1 Ole John Nielsen: "Atmospheric Chemistry of nitrogen containing species". EUROTRAC workshop, Paris, 2nd-4th February 1988.

5.2 Ole John Nielsen and Peter Bo: "COLUMN2 - A computer program for simulating migration". CHEMVAL meeting, Paris, 10th May 1988.

5.3 Ole John Nielsen, Jack Treacy, Denis O'Farrell, Michael Donlon and Howard Sidebottom: "Reaction of OH with nitroalkanes". Kemisk Forening, Odense University, Odense, 7th June 1988.

5.4 Ole John Nielsen, Howard Sidebottom, Jack Treacy and Denis O'Farrell: "Gas phase reactions of OH with nitroalkanes". 9th Danish Polish symposium on radiation chemistry, Risø, 6th-9th June 1988.

5.5 Ole John Nielsen, Jack Treacy, Denis O'Farrell, Michael Donlon and Howard Sidebottom: "Kinetic and mechanism for the reaction of hydroxyl radicals with nitrogen containing compounds". 10th International symposium on gas kinetics, University College of Swansea (UK), 24th-29th July 1988.

5.6 Ole John Nielsen: "Gas phase kinetic studies at Risø National Laboratory". Ford Motor Company, Dearborn (SA), 21st July 1988.

5.7 Ole John Nielsen: "The study of the reaction of OH with nitroalkanes". COST611 WP2 meeting, Norwich, 20th-23rd September 1988.

5.8 Ole John Nielsen: "Gas phase kinetics and atmospheric chemistry". H.C. Ørsted Institute, Copenhagen, 27th October 1988.

5.9 Ole John Nielsen: "Studies of atmospheric reactions using pulse radiolysis". Forskerseminar om luftforurening, -deposition, atmosfærekemi og -fysik, Risø, 16th-17th November 1988.

5.10 Robert Wilbrandt: "Lasers and Laser Spectroscopy". Forskerkursus på NBI, 20th April 1988.

5.11 Robert Wilbrandt: "Experimental and theoretical studies of hexatriene vibrations in the lowest excited triplet state". Invitet lecture at Kemisk Forenings Årsmøde, 7th June 1988.

5.12 Robert Wilbrandt: "Experimental and theoretical studies of hexatriene vibrations in the lowest excited triplet state". Invitet lecture at Euchem Conf. Photoisomerism and Rotamerism, Assisi, Italy, 13rd July 1988.

5.13 Robert Wilbrandt: "Retinal Photochemistry". University of Bologna, 11st July 1988.

5.14 P. Pagsberg, E. Ratajczak and A. Sillesen: "Kinetics of Methyl Radicals studied by Pulse Radiolysis combined with time-resolved infrared diode laser spectroscopy. Presented at CEC Combustion Kinetics Symposium, Perugia, Italy, September 1988.

5.15. A. Sillesen: Pulse Radiolysis facilities at Risø for studies in gas

phase kinetics. More detailed about the performance of the new tunable diode laser system for infrared absorption measurements." Department of Physical Chemistry, Wroslaw Univesity, Sept. 1988.

5.16 K.J. Olsen and J.W. Hansen: "Kalibreringssammenligning af høj-energifoton- og electrobeams ved hjælp af alanin dosimetre". Dansk Selskab for Onkologi, Århus, 24th April 1988.

5.17 J.W. Hansen: "Low- and High-LET particle dosimetry by ESR spectrometry of amino acids". National Bureau of Standards, Gaithersburg, MD 20899, USA, 18th August 1988.

5.18 J.W. Hansen: "Alanine, a tissue-equivalent free radical dosimeter for low- and high-LET radiation". Brookhaven National Laboratory, Upton, L.I., New York, 23rd August 1988.

5.19 K.J. Olsen, J.W. Hansen and M.R.P. Waligorski: "ESR dosimetry in calibration comparisons of high energy photons and electrons". Second Int. Symp. on ESR Dosimetry and Application, Munich-Neuherberg, 10-13th October 1988.

5.20 P. Hjortenber, J.W. Hansen and M. Wille: "Measurements of dose rate from Ru-106/Rh-106 opthalmic applicators by means of polymer-alanine foils and MgBO₄:Dy TL-dosimeters". Second Int. Symp. on ESR Dosimetry and Applications. Munich-Neuherberg, 10-13th October 1988.

5.21 J.W. Hansen and K.J. Olsen: "Predicting Decay in Radical Concentration on L-Alpha Alanine following high-LET Exposures". Second Int. Symp. on ESR Dosimetry and Applications. Munich-Neuherberg, 10-13th October 1988.

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